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# Nanocomposite of CdS particles in polymer rods fabricated by a novel hydrothermal polymerization and simultaneous sulfidation technique

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**A hydrothermal polymerization and simultaneous sulfidation (HPSS) process and the mechanism for the fabrication of one-dimensional (1-D) nanocomposites of well dispersed CdS nanoparticles self-assembled in the polymer nanorods is presented.**

Low dimensional, especially 1-D arrays of metal and semiconductor nanoparticles, owing to their potential applications in optical and electronic sensors,[1,2] nanoscale electronics,[2,3] and catalysis,[4] are receiving extensive attention. The synthesis and characterization of such materials, especially of inorganic–polymer nanocomposites has aroused much research interest.[5–7]

Many methods have been applied to prepare semiconductor–polymer nanocomposites with different sizes and/or morphologies. Meissner *et al.*[8] first reported a system involving dispersed semiconductor/polymer arrangements by physically embedding monograin CdS particles of *ca.* 40 μm diameter in a thin, non-conducting polyurethane membrane and various photoprocesses were examined. Marinakos *et al.* synthesized interconnected arrays of Au/polypyrrole colloids of 1-D morphology using $Al_2O_3$ membranes as the template.[9] However, few reports have appeared regarding the synthesis of coupled 1-D nanoparticle systems. Notable exceptions are 1-D strands of iron oxide particles used for navigation by magnetotactic bacteria,[10] self-organized 1-D CdS chains observed by Chemseddine *et al.*,[11] and dithiol-linked CdSe dimers and DNA-linked Au trimers synthesized by Alivisatos *et al.* [12]

Polymers have advantages over other templates due to the maintenance of the superstructures of the monomers during the polymerization. Thus, a series of inorganic–polymer composites with different sizes and morphologies can be synthesized.[13] Here we report a novel hydrothermal polymerization and simultaneous sulfidation (HPSS) process to fabricate 1-D CdS nanoparticle/poly(vinyl acetate) (PVAc) nanorod composites. This method is based on the mechanism that the polymerization of organic monomers and the formation of the CdS nanoparticles simultaneously take place in aqueous solution. The CdS nanoparticles were well dispersed in the PVAc nanorods to form 1-D composites.

In a typical experiment, 0.005 mol thioacetamide (taa) was added to 50 ml $2 \times 10^{-2}$ mol $l^{-1}$ $CdCl_2 \cdot 2.5H_2O$ aqueous solution in a Teflon lined autoclave of 60 ml capacity. Then 0.4 ml vinyl acetate (VAc) was added to the above solution. 0.008 g of 2,2′-azobisisobutyronitrile (AIBN) as initiator was then added. The autoclave was maintained at 80 °C for 12 h then allowed to cool to room temperature. The products were filtered off and washed with distilled water and absolute ethanol, dried in a vacuum at 60 °C, and collected for further characterization.

Powder X-ray diffraction (XRD) patterns for the products were collected on a Japan Rigaku D/max-γA diffractometer equipped with graphite-monochromatized high-intensity Cu-Kα radiation ($\lambda$ = 1.51478 Å) at a scanning rate of 0.02° $s^{-1}$ in the $2\theta$ range 10–70°. IR spectra were measured on a Bruker Vector-22 FT-IR spectrometer from 4000 to 400 $cm^{-1}$ at room temperature. Samples were ground with KBr and pressed into pellets. UV–VIS absorption spectra were recorded on a Shimadzu UV-2100 spectrophotometer scanning from 700 to 300 nm at room temperature with ethanol as the reference. TEM images were taken on a Hitachi H-800 transmission electron microscope, using an accelerating voltage of 200 kV. The samples were dispersed in absolute ethanol ultrasonically, then the suspension was dropped onto copper grids coated with amorphous carbon film.

A representative XRD pattern is shown in Fig. 1. All the diffraction peaks can be indexed to the wurtzite structure CdS with cell constants $a_0$ = 4.136, $c_0$ = 6.713 Å. The values are close to those in the JCPDS card (card No. 41-1049). Applying the Scherrer equation, the average crystallite size was estimated to be 10 nm. Although there is no apparent broad peak corresponding to the polymer matrix in the XRD pattern, which may be due to the low content of PVAc in the final product and the low crystallinity of PVAc, the existence of PVAc was fully verified by FT-IR spectroscopy. The presence of PVAc in the 1-D nanocomposite was also detected in TEM micrographs.

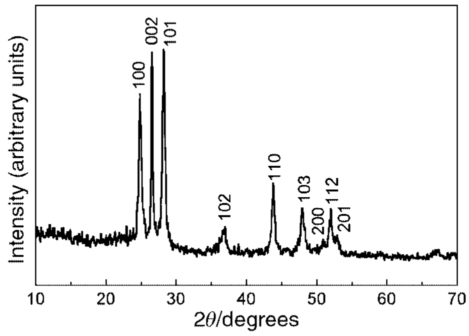

**Fig. 1** XRD pattern of a CdS nanoparticle/PVAc nanorod composite fabricated by the HPSS technique at 80 °C for 12 h.

A representative FT-IR spectrum of a sample is illustrated in Fig. 2. The peak at 1739.4 $cm^{-1}$ ($\upsilon_{C=O}$), and characteristic peaks at 1239.9, 1020.9 $cm^{-1}$ ($\upsilon_{C-O}$), and 1375.7 $cm^{-1}$ ($\delta_{CH_3}$) corresponding to PVAc are clearly seen. The IR spectrum is similar to the standard IR spectrum curve of PVAc (Sprouse collection of IR, card No. 187–189) and distinctly different from that of the VAc monomer (Standard IR Grating Spectra,

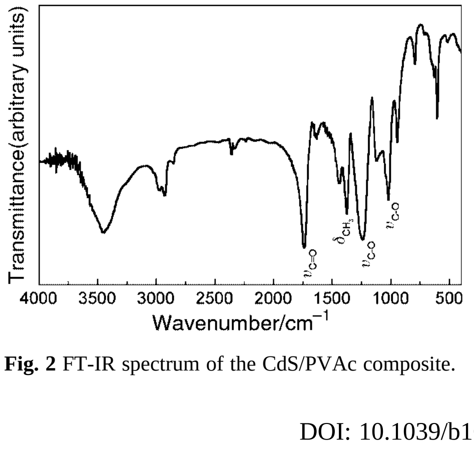

**Fig. 2** FT-IR spectrum of the CdS/PVAc composite.

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card No. 8112), which indicates the successful polymerization of VAc and confirms the existence of PVAc in the final product.

Fig. 3 shows a typical TEM micrograph of nanorods in the CdS/PVAc composite. The image shows that the nanorods are *ca.* 75 nm in width and several hundred nm in length. The average crystalline size for the CdS particles in the polymer nanorods is *ca.* 13 nm, well consistent with that calculated by the Scherrer equation from half-widths of the diffraction peaks. Because polymers show low contrast in TEM micrographs, light areas in the spaces among the CdS nanoparticles suggest the existence of PVAc in the composite.

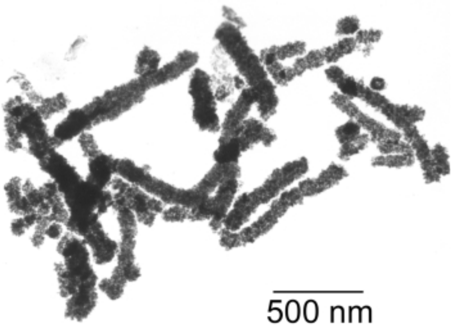
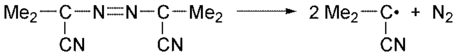


**Fig. 3** TEM micrograph of the CdS/PVAc nanocomposite.

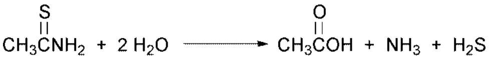
According to a typical UV–VIS spectrum, the wavelength of the maximum absorption peak, $\lambda_{\max}$, for the CdS nanoparticles in the CdS/PVAc nanorod composite is at *ca.* 478 nm, which is blue shifted relative to that for bulk CdS, 515 nm.[14] This can be explained as due to a size confined effect as a result of the tiny dimensions of the nanoparticles in the CdS/PVAc composite.

It is well known that the radical initiator AIBN decomposes at 45–65 °C, according to eqn. (1).

 (1)

$$\mathrm{Me_2{-}\underset{CN}{\underset{|}{C}}{-}N{=}N{-}\underset{CN}{\underset{|}{C}}{-}Me_2} \longrightarrow 2\,\mathrm{Me_2{-}\underset{CN}{\underset{|}{C}}{\bullet}} + \mathrm{N_2} \qquad (1)$$

The produced radicals initiate the polymerization of VAc. Accompanying the polymerization, CdS nanoparticles are also simultaneously formed by the hydrolysis of taa as described in eqns. (2) and (3).

 (2)

$$\mathrm{CH_3\overset{S}{\overset{||}{C}}NH_2} + 2\,\mathrm{H_2O} \longrightarrow \mathrm{CH_3\overset{O}{\overset{||}{C}}OH} + \mathrm{NH_3} + \mathrm{H_2S} \qquad (2)$$

$$\mathrm{Cd^{2+}} + \mathrm{H_2S} \longrightarrow \mathrm{CdS} + 2\,\mathrm{H^+} \qquad (3)$$

The formation of VAc emulsions, the subsequent maintenance of the superstructure by polymerization, the simultaneous sulfidation of $\mathrm{Cd^{2+}}$, and the sticking of polymer spheres explain the self-assembly of the 1-D CdS nanoparticles/PVAc nanorod composites. In 1962, a spherical morphology of PVAc was reported by Napper, *et al.* when the monomer, VAc, was polymerized thermally.[15] Computer simulations of the development of rodlike semiconductor–polymer hybrids from hybrid spheres was reported by Stoll and Buffle.[16] In the present HPSS process, VAc emulsions are formed in aqueous solution.[17] At the same time, $\mathrm{Cd^{2+}}$ cations originally coordinated to carboxyl groups in the monomer react with released $\mathrm{S^{2-}}$ to form CdS clusters. With increasing reaction time, VAc emulsions are polymerized into PVAc spheres. Owing to their glutinosity the PVAc spheres stick together to form polymer nanorods. The increasing viscosity of these polymer nanorods inhibit growth of the CdS nanoparticles. This mechanism is further suggested by the fact that spherical CdS/PVAc nanocomposites are observed in samples reacted for only short reaction times.

In summary, a hydrothermal polymerization and simultaneous sulfidation (HPSS) process to prepare CdS nanoparticle/poly(vinyl acetate) nanorod composites has been presented. CdS nanoparticles of *ca.* 10 nm were self-assembled and well dispersed in the nanorods of PVAc to form 1-D nanocomposites. The experiments indicated that the 1-D morphology was favored by agglomeration of several PVAc spheres. The polymerization of VAc turns the VAc emulsions into polymer spheres and prevented further growth of CdS nanoparticles. The present HPSS technique may provide a new route to prepare other 1-D metal sulfide semiconductor–polymer hybrid nanocomposites.

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